k-Space Characterization of Electronic States in AlPdMn Icosahedral Quasicrystals

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INTRODUCTION

Quasicrystals display near-perfect x-ray diffraction patterns, despite having an aperiodic crystalline order. Indeed, they display point-group rotational symmetries (5-fold, 8-fold, etc.) which are incompatible with long-range periodicity. In view of their intriguing symmetries and their (for a metallic alloy) unusual physical properties, these materials have received an enormous amount of theoretical and experimental attention since their discovery in 1984 by Schechtman et al.[1] Such has been the impact of these exotic materials that the very definition of crystallinity has recently been rewritten to include this family of alloys. An interesting aspect of quasicrystals is that their x-ray diffraction patterns, which sample the structure in reciprocal (momentum) space, retain the property of forbidden rotational symmetry combined with aperiodic translational order. Thus one might speculate that similar scattering of valence electrons occurs as well, leading to the formation of electronic bands. However, the response of the valence electrons to the unusual symmetry of the lattice is difficult to predict. Whether these states are localized, extended, or in a critical state between the two has yet to be resolved;[2] the best formalism for calculating their electronic states is still to be determined. In this study we use the well established method of angle-resolved photoemission to investigate the electronic states in quasicrystals with a view to determining whether they are localized or extended, i.e. free-electron-like. We clearly demonstrate the itinerant nature of the valence states in AlPdMn quasicrystals. Our results show that the electron states exhibit the symmetry and aperiodicity of the quasicrystals.

EXPERIMENT

Surface preparation of single-grain AlPdMn wafers, characterized with low energy electron diffraction (LEED) and core-level photoemission, followed the sputter/anneal procedure of Thiel et al. We believe our surfaces are quite close to the bulk in structure, a fact which was confirmed by comparing the stoichiometry and valence density of states between the as-prepared surfaces and surfaces prepared by cleaving. The LEED results were similar to those of Thiel et al.,[3] and the core-level photoelectron diffraction patterns were identical to those presented by Aebi et al.[4] Surface preparation and angle-resolved photoemission measurements were performed *in situ* at BL7.0 at the ALS, with combined instrumental energy resolution ~50 meV and with angular acceptance better than ~1.4 degrees. All measurements were obtained at room temperature. In our setup the sample's polar angle θ and azimuthal angle ϕ are varied, while the angle between the incident photon beam, the electron analyzer, and the sample's polar axis remain fixed.

We present three major conclusions from the energy- and angle-resolved photoemission results:

(1) <u>Demonstration of quasicrystal bandstructure</u>. Fig. 1(a) shows a series of angle-resolved photoemission spectra obtained at photon energy hν=100.0 eV. The lower spectrum, (thick solid line) obtained by averaging the angle-resolved spectra, simulates the total spectral density of states. The angle-resolved spectra in Fig. 1(a), deviate significantly from the integrated spectrum. Clear angular-dependent features occur in addition to the fixed integrated spectrum. To bring out these weaker features, we present in Fig. 1(b) the per cent deviation between the angle-resolved spectra and the fixed spectrum. Several groups of peaks are apparent. From the systematic shifts of these peaks with angle, we deduce that their binding energies exhibit dispersion with angle and thus with parallel electron momentum $k_\parallel$. To highlight this energy dispersion of the peaks in our data, we have plotted the data as an intensity map in Fig. 1(c). The states were plotted in the conventional bandmapping fashion as binding energy vs. electron momentum $k_\parallel = 0.5124\sqrt{\hbar\omega}\sin\theta$ parallel to the surface. It is quite clear that they display large bandwidths of up to 2 eV, which is on the order of bandwidths found commonly in metals. Thus we confirm the existence of electronic bands in i-AlPdMn.
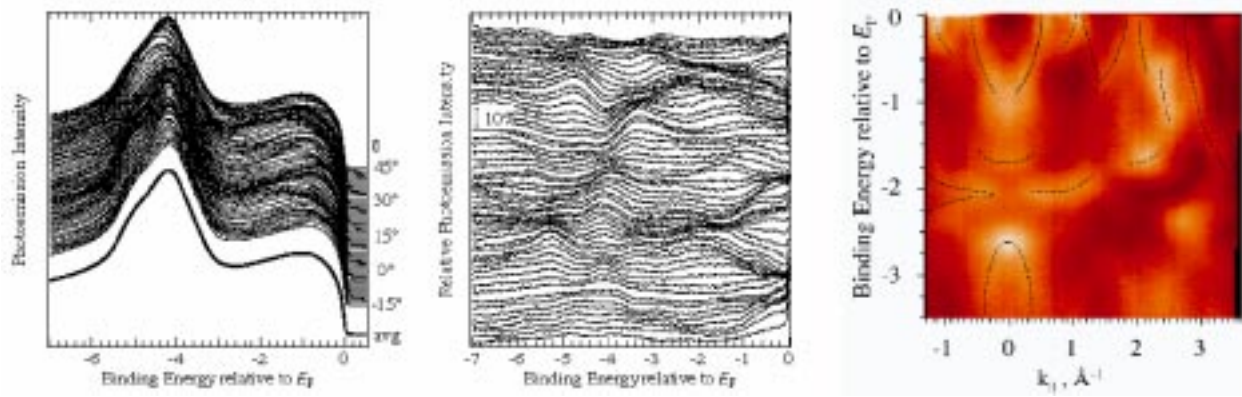

Figure 1. (a) Valence band spectra as a function of angle q. The angle-averaged spectrum is shown below (darker line). (b) Relative deviation between the angle-resolved and –integrated spectra. (c) Intensity plot of the same data, plotted as Energy vs $k_\parallel$.

(2) <u>Rotational Symmetry of the bands</u>. A characterization of valence states in i-AlPdMn as a function of both azimuthal and polar angle demonstrates that they have 5-fold rotational symmetry. Figure 2 shows a polar intensity map, in which the radius is proportional to the polar angle θ, and where the angle in the images represents the azimuth angle ϕ. Fig. 2(a) shows raw data, which was acquired by fixing the electron energy to the Fermi edge, and rotating the sample through the ranges $-115° < \phi < 115°$ degrees and $\theta < 45°$. (The intensity variation along the dashed line in Fig. 2(a) is the same as that at the Fermi edge in Fig. 1(a).) As the superimposed pentagon indicates, the data show a fivefold rotational symmetry, which is in agreement with the diffraction data for this quasicrystal orientation. The fivefold symmetry is already quite evident in the raw data, but fivefold symmetrization followed by smooth background subtraction (Fig. 2(b)) reduces experimental noise, and demonstrates the existence of sharply defined features in $k_\parallel$-space. A stack of such plots for three different binding energies, the top one right at E_F (Figure 2(c)) reflects the observation, that the photoemission features have five-fold symmetry at all electron binding energies.
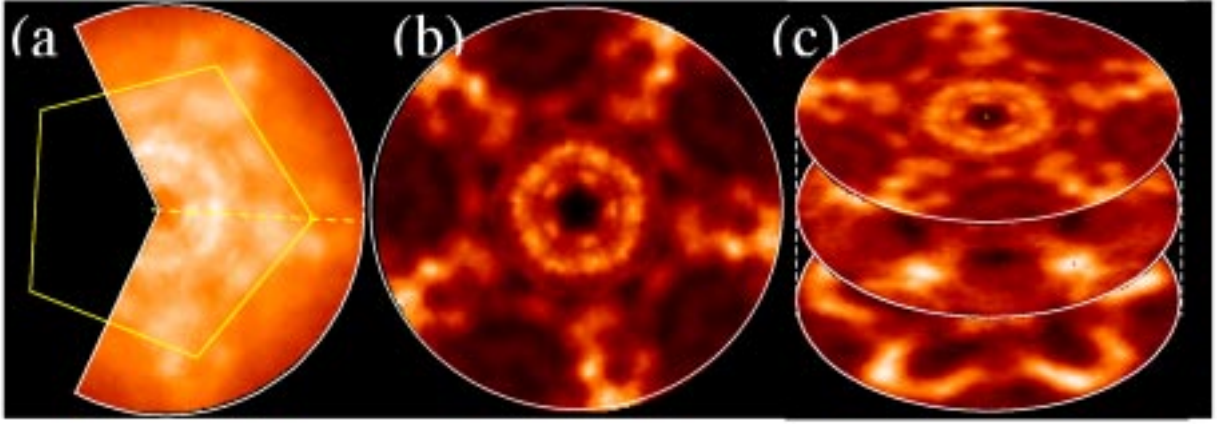
Figure 2. Constant-binding-energy surface (near the Fermi level) emission profile. (a) raw data; the pentagon indicates the 5-fold symmetry. Data along the dashed line in (a) is the same as the data along the Fermi level in Fig. 1. (b) symmetrized and background-subtracted data. (c) A sampling of data for three different binding energies; a total of 96 energy channels was acquired.

(3) <u>Measurement of the Aperiodic Fermi Surface</u>. The region around E_F encompasses the so-called pseudogap, which is thought to directly relate to the unusual physical properties of the quasicrystals. Detailed measurements of this energy surface in 3-dimensional k-space should provide great insight into the quasicrystal electronic properties, as well as provide a stringent test for theoretical models. By way of comparison, we first present such Fermi surface for a normal, periodic metal (Ag(100) surface) in Fig. 3(a). The lines represent the Brillouin zone boundaries as derived from the lattice constant of Ag and the known orientation of the crystal. That the Ag sp states near E_F obey the symmetry of the fcc reciprocal lattice is obvious, and the bright features with the shape of a truncated square correspond to the Fermi level crossings of the sp band. A similar set of data for i-AlPdMn is shown in Fig. 3(b) for a similar range of k values. The data are markedly different from crystalline Ag, in that no repetition of features along $k_\perp$ or $k_\parallel$ occurs. While there is an apparent symmetry of features around $k_\perp$, there is no repetition of features for larger values of $k_\parallel$.

In summary, we have observed a fivefold symmetric pattern of valence states in i-AlPdMn, which in itself demonstrates that these state feel the point symmetry of the quasicrystal. Clearly dispersing features in the valence level spectrum show that these states are bandlike in nature,
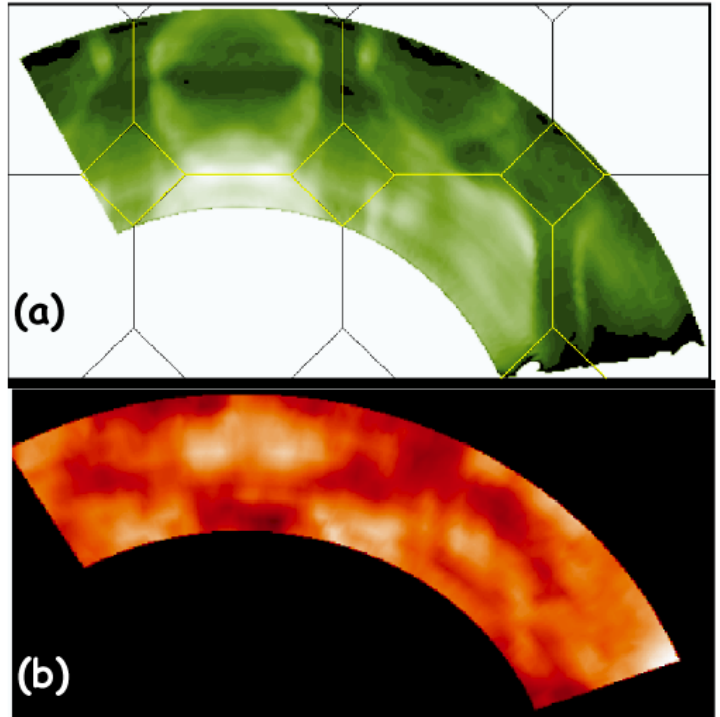

Figure 3. (a) The fermi surface of Ag(100), a normal, periodic crystal. Fermi-edge intensity is shown as a function of $k_\perp$ vs $k_\parallel$ (horizontal axis). (b) Fermi-edge data for i-AlPdMn quasicrystal, for a similar k-range as in (a).

and that these bands extend up to and beyond the quasigap. States near the Fermi edge exhibit a markedly different pattern in three-dimensional *k*-space from that observed in regular crystals, suggesting that the symmetry of valence level states is not only affected by the immediate atomic environment, but that they are also affected by the long range quasicrystalline atomic arrangement.

ACKNOWLEDGMENTS

REFERENCES

[1]D. Schechtman et al, Phys. Rev. Lett. 53, 1951 (1984).
[2]See. e.g., C. Janot, Quasicrystals, a Primer, 2nd edition. Oxford, 1994.
[3]Z. Shen et al, Phys. Rev. B 58, 9961 (1998).
[4]P. Aebi et al, unpublished.

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